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OBSERVATIONS *and* EXPERIMENTS *undertaken with a view to determine the* QUANTITY *of* SULPHUR *contained in* SULPHURIC ACID; *and of this* LATTER *contained in* SULPHATES *in general.*

By RICHARD CHENEVIX, *F. R. S. and M. R. I. A.*

Read, May 4, 1801.

IN a paper which I had the honour to preſent to the Royal Society of London, and the ſubject of which was the analyſis of ſome arſeniates of copper, and of iron, I had occaſion, in examining many pyrites, matrices of thoſe ores, to remark the very great inequality which prevailed in the reſults of repeated experiments, made with a view to determine the proportion of ſulphur. But I ſoon perceived, that the inaccuracy was cauſed by a partial combuſtion and acidification of the radical, through the means of the nitric acid, employed to diſſolve the ore.

HAVING therefore, in the uſual manner, aſcertained what quantity of that ingredient remained untouched, I was forced to ſeek the reſt of it in the liquor, which had waſhed the various precipitates. To obtain it, I poured a ſolution of nitrate of Barytes into thoſe waſhings, when all the other ſubſtances had been carefully ſeparated, and was thereby enabled to precipitate, in a ſtate of purity, the ſulphate of Barytes, formed by that earth, and by the portion of ſulphur originally acidified, in the firſt treatment of the ore by nitric acid. To come at the knowledge of the proportion of ſulphur, contained in a given quantity of ſulphate of Barytes, I had recourſe, in the firſt inſtance, to the quantity of ſulphur, ſaid by Lavoiſier to be contained in ſulphuric acid, and, in the next, to the proportions of the latter, announced in the ſynoptic tables of Fourcroy, as entering into the compoſition of ſulphate of Barytes. According to the former of thoſe chymiſts, 100 parts of ſulphuric acid contain 71 of ſulphur and 29 of oxygen; and again, in adopting the proportions of the latter, we have 33 per cent. of acid, on ſulphate of Barytes. But if 100 contain 71 of ſulphur 33 muſt contain 23.43. Conſequently, for every 100 parts of ſulphate of Barytes, I was to allow 23.43 of ſulphur. But, by the reſults of my analyſes, I had ſuch quantities of ſulphate of Barytes, as induced me to doubt the accuracy of one or other of the ſtatements, by which I eſtimated the quantity of real ſulphur contained in the ore.

No perſon is better acquainted than our celebrated Preſident, with the many difficulties that occur in the analyſis of ſalts in general; particularly with regard to the quantity of real acid they may contain. It has been a work of trouble to the ableſt chymiſts, and they have not always agreed in their reſults. The proportions, announced by Fourcroy, may therefore be doubted, in common with thoſe of the other learned operators, to whom I have alluded.

The real quantity of acid, produced by the combuſtion of any acidifiable baſis, can be determined by one or other of the following methods only: by direct combination, in ſome ſalt, the proportions of which are already known; or by obtaining, in a ſtate perfectly free from water, the acid reſulting from ſuch combuſtion. To the former method, the general objections againſt all analyſes of ſalts muſt apply. The latter is ſtill more defective. It is by no means certain, that we have ever yet obtained any acid, in a ſtate of perfect ſiccity, unleſs we except the phoſphoric and the arſenic; for even the cryſtallized vegetable acids retain a portion of water in their cryſtallization. It is not that I abſolutely deny our having obtained them ſo; but I ſay merely, that we have no proof. It would indeed be ſetting narrow bounds to the perfection of nature, to aſſert, that no combuſtible body could, when ſaturated with oxygen, aſſume, of itſelf, the ſtate of liquidity; or that the oxide of the particular ſubſtance, called hydrogen, muſt be preſent to confer that property. Doubtleſs, ſulphuric acid may, as well as water, contain, in itſelf, ſo juſt a proportion of ſpecific heat, as to remain liquid at the temperature of our globe, and under the preſſure of our atmoſphere. But, both water and ſulphuric acid being eaſily volatilized, and having a powerful affinity for each other, it is not eaſy, if even poſſible, by diſtillation, to ſeparate them with ſufficient accuracy, in experiments of delicate inquiry. A ſecond ſource of error, therefore, remained open in this branch of the calculation, which gave the proportion of 23.43 of ſulphur, as that contained in 100 parts of ſulphate of Barytes.

However, before I would allow myſelf to call in queſtion ſuch authorities as thoſe I have quoted, I inſtituted the following experiments: In a tubulated glaſs retort, I put 100 parts of purified ſulphur, and poured upon them ſtrong nitric acid. A quilled receiver, plunging into a Woulfe's apparatus, was adapted to the retort; and, all being well luted, I proceeded to diſtil. The liquor, which came over, was poured back ſeveral times upon the ſulphur, until the whole was diſſolved. The water, which had come over, and that, through which the nitrous gas, produced during the operation, had paſſed, were eſſayed for ſulphureous acid, and no traces of it could be found. No ſulphur had been volatilized; therefore no ſuſpicion could remain, that all was not converted into ſulphuric acid. The liquors, which were in the various parts of the apparatus, were united; and to them was added a ſufficient quantity of nitrate of Barytes. The whole was evaporated gently; becauſe, though I am well acquainted with the very little ſolubility of ſulphate of Barytes, I well know that nitric acid will retain a ſmall portion of it, particularly when formed in a liquor where that acid abounds. In a firſt experiment, I obtained 694 from 100 of ſulphur, in a ſecond, 348 from 50, and in a third, 347 from the ſame quantity. But the ſimple rule of three reduced theſe quantities to 14.6, or 14.4 per cent. of ſulphur, contained in ſulphate of Barytes; a difference wholly to be neglected. If, therefore we take 14.5 as the average, for the quantity of ſulphur contained in 100 parts of ſulphate of Barytes, we ſhall not be far from the truth. From the accordance of theſe experiments, repeated and varied, I had now no doubt, but concerning the ſource where I was to ſeek the error, which gave 23.43 as the juſt proportion.

To aſcertain this point, I operated in the following manner: I prepared ſome lime, as pure, I believe, as chymical means can procure it. I digeſted white marble in muriatic acid; and,

by

by leaving an exceſs of the earth, was certain, that by the ſuperior affinity of lime for that acid, nothing elſe had been taken up. Upon trying the ſolution with ammonia, no precipitate took place. By means of carbonate of potaſh, I ſeparated the lime in the ſtate of carbonate; and, after well waſhing the precipitate, expoſed it in a platina-crucible to a violent heat, till the weight no longer diminiſhed. I am acquainted with no more efficacious method to prepare lime, fit for the delicate purpoſes of ſcientific chymiſtry.

One hundred parts of this lime were diſſolved in dilute muriatic acid, in the ſame platina-crucible, previouſly weighed; and then ſulphuric acid was added in ſufficient quantity. Sulphate of lime was precipitated; and the veſſel was expoſed to a heat, at firſt gentle, to evaporate the liquor; and then, by degrees, raiſed to a temperature, which could expel every thing but the combined ſulphuric acid, and leave the ſulphate of lime completely calcined. The crucible with the ſalt was then weighed and the augmentation was 76.—It appears to me, that, if we admit (and I ſee no reaſon that we ſhould not admit it) that calcined lime and calcined ſulphate of lime are wholly exempt from water, it muſt be clear, that the 76 additional weight were ſulphuric acid; and, that the ſulphuric acid muſt in this ſtate, more than in any other, approach nearer to what may be termed, abſolutely real acid. One hundred parts of calcined ſulphate of lime contain therefore

Lime - - -	57
Sulphuric acid - - -	43
	100

By the former experiments (thoſe made upon ſulphur converted into acid, and then united to Barytes) we had the quantity of ſulphur, contained in ſulphate of Barytes. By the latter (thoſe made by directly combining lime with ſulphuric acid) we had the proportion of real acid, contained in calcined ſulphate of lime. Conſequently, by knowing the ratio, that ſulphate of Barytes bears to ſulphate of lime, with regard to the acid in each, we ſhall arrive at the knowledge of the quantity of ſulphur, contained in real ſulphuric acid. For this purpoſe, I attempted to diſſolve, in water, 100 parts of ſulphate of lime. But finding, in this method of proceeding, a conſiderable inconvenience ariſing from the great quantity of liquor, neceſſary to effect the ſolution of that ſalt, I had recourſe to the following expedient. Upon 100 grains of calcined ſulphate of lime, I poured ſome oxalic acid, which attracts the baſis with an affinity ſuperior to that exerciſed by ſulphuric acid. Oxalate of lime was here formed; but oxalate of lime is ſoluble in a very ſmall exceſs of any acid. A little muriatic acid operated a com-

plete

plete ſolution; and thus a great quantity of ſulphate of lime required but little water to diſſolve it. Into this liquor, muriate of Barytes was poured, and ſuffered to remain ſome time, gently heated. By theſe means, any oxalate of Barytes, that might have been formed, was retained in ſolution, by the original exceſs of acid; and the entire quantity of ſulphate of Barytes was depoſited. Of the exactneſs of all theſe methods, which I uſed, as the inſtruments by which I aſcertained theſe reſults, I convinced myſelf by various preliminary experiments. After the uſual filtration, waſhing and drying at the gentle heat of a ſand-bath, I obtained in one experiment 185, in another 183, and, laſtly, in another 180. This difference does not exceed the limits of what all perſons, converſant in analytic chymiſtry, will allow to experiments of this nature. We may therefore take 183 as the mean proportion; conſequently, we ſhall ſay, that 183 of ſulphate of Barytes contain the ſame quantity of ſulphuric acid, as 100 of ſulphate of lime; and 183 : 43 :: 100 : 23.5. Therefore 23 5 is the proportion of acid in 100 of ſulphate of Barytes. But we have before ſeen, that 14.5 of ſulphur, acidified by nitric acid, form that portion of ſulphuric acid contained in 100 of ſulphate of Barytes: viz. 23.5. We muſt now ſay, that 23.5 : 14.5 :: 100 : 61.5, and the fourth term will be the proportion of ſulphur = 61.5, which combined with 38.5 of oxygen will form 100 of real ſulphuric acid.

In neither of the proportions, whether it be of the acid contained in the ſalt, or of the combuſtible baſis contained in the acid, do I agree with the two chymiſts whom I have quoted. This juſtly excited ſome doubts in my mind, and led me to repeat my experiments. Nor ſhould I yet be thoroughly ſatisfied, if I could not, upon other grounds, than by ſuppoſing inaccuracy in them, account for the apparent differences. We muſt ever expect to ſee the errors of our predeceſſors corrected by men, much inferior in abilities; but who, by poſſeſſing more certain means, ſupply the want of genius and invention. At the time in which the experiments were made, that determined the proportion of 33 per cent. of ſulphuric acid in ſulphate of Barytes, it was not known that we had never obtained any Barytes pure; and that a conſiderable portion of carbonic acid reſiſted the action of every degree of heat that had been applied to carbonate of Barytes. The fact was, I believe, firſt obſerved by Pelletier; but the method of avoiding the inconvenience was pointed out by Vauquelin. He decompoſes nitrate of Barytes by lime, and a moderate degree of heat is ſufficient to expel all the acid and the water. The chymiſts, I have mentioned, performed ſynthetic experiments, by combining, directly or indirectly, ſulphuric acid, and ſuch Barytes as they imagined to be pure. The conſtant ſimilarity of their reſults is ſufficient to prove the accuracy of their operations; but working upon an impure ſubſtance, they muſt have been contented with a ſimilarity of error.

THREE cauſes may exiſt which are capable of accounting for any variation, whether in *plus* or in *minus*, that might have appeared in the experiments, by which Lavoiſier determined the quantity of ſulphuric acid, obtained by the combuſticn of ſulphur in oxygen gas.

1ſt. A part of the ſulphur may be volatilized during combuſtion.

2d. ALL the Sulphur may not be converted into ſulphuric acid; but part may remain in the ſtate of ſulphureous acid.

3d. In rectifying, ſome acid may come over along with the water; or, *vice verſâ*, ſome water remain with the acid. Theſe conſiderations will excuſe me for having propoſed a doubt, where the authority of ſo great a man exiſts againſt the experiments which I have related.

THE method which I had uſed to aſcertain the quantity of ſulphur in an ore, had been practiſed by Taſſaert, (Annales de Chimie, No. 82: Analyſis of Cobelt from Tunaberg) but he calculated according to the proportions of Lavoiſier and of Fourcroy. In another paper by Thenard, (Annales de Chimie, No. 96.) he ſtates the proportions of ſulphuric acid, obtained by treating ſulphur with nitric acid, to be

Sulphur	- -	55.56
Oxygen	- -	44.44
		100.00

but in the extract given by Guyton in that No. of the Annales de Chimie, the mode of operation is not deſcribed. Calcined ſulphate of Barytes is eſtimated in the ſame paper to contain

Barytes	- -	74.82
Sulphuric acid	- -	25.18
		100.00

which proportions are as near to what I had found as can be expected; for ſulphate of Barytes does not contain more than 3 per cent. of water of cryſtallization, and they muſt be deducted from the quintal.

Having determined with accuracy the proportion of acid in any inſoluble ſulphate, it is eaſy to proced to the determination of that contained in any other ſulphate. The docimaſtic art or analytic chymiſtry, in general, cannot however expect to derive ſuch advantages from the knowledge of ſoluble ſalts, as of thoſe, which, from their inſolubility, may be uſed with accuracy in delicate experiments to determine the proportions of the conſtituent parts of bodies. But if, with this mode of operating, we compare the quantities of real acid, ſaid (in thoſe excellent tables with which Mr. Kirwan has enriched the ſcience) to be contained in ſulphuric acid of different ſpecific gravities, they will ſerve as proofs of their mutual validity; and perhaps demonſtrate, that ſulphuric acid, as well as water, and ſome other bodies, may of itſelf enjoy liquidity, at the temperature and preſſure which act upon our globe.